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(54) **Direct hydrogenation process for glyceride oil.**

(57) The invention relates to a hydrogenation process for glyceride oil characterised by a control of moisture content of the reaction mixture comprising the steps of:

- i) selecting a glyceride oil comprising less than 60 mg P/kg oil;
- ii) carrying out the hydrogenation treatment by
 - a) contacting the glyceride oil with hydrogen in the presence of a hydrogenation catalyst
 - b) saturating partially the initially available double bonds in the glyceride oil and
 - c) removing the catalyst;

wherein the hydrogenation treatment being positively controlled by intentionally maintaining the moisture content of the reaction mixture comprising oil, hydrogenation catalyst and hydrogen, below 0.2% by weight calculated on the weight of the mixture; and

- iii) optionally, purifying the hydrogenated oil from remains of catalyst.

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The present invention relates to a hydrogenation process for unsaturated glyceride oil, in particular to a hydrogenation process for direct, selective and partial hydrogenation of unsaturated glyceride oil with optionally concomitant cis/trans isomerization of the glyceride oil. The hydrogenated or hardened oils obtained are specifically used for the production of margarines and shortenings. The process is particularly useful for the hardening of vegetable oils which contain per kg oil less than 60 mg phosphorus (denoted as 5 60 ppm P) in the form of phosphatides.

Crude glyceride oils are normally subjected to a so-called degumming treatment in order to remove phosphatides from the glyceride oil. In conventional degumming processes, water is added to the crude glyceride oil to hydrate the phosphatides which are subsequently removed by for instance centrifugal 10 separation. Since The resulting degummed oil often still contains unacceptably high levels of "non-hydratable" phosphatides, which may interfere with subsequent oil processing including hydrogenation. Therefore the water-degumming treatment is normally followed by a chemical treatment with acid and/or alkali in order to remove the residual phosphatides and to neutralize the free fatty acids. This subsequent treatment is often called alkali refining. The soapstock formed is separated from the neutralized oil. During 15 further refining the oil may be bleached resulting in a neutralized bleached oil containing 0-5 ppm P. If desired, the oil is subsequently hydrogenated. A deodorizing treatment is a usual last step of refining.

US-A-4,049,686 discloses a degumming method in which crude or water-degummed oil is treated with a concentrated acid, such as citric acid, and residual phosphorus level can be brought down to within the range of 20-50 mg P/kg oil. This degumming method is a so-called super-degumming method.

A refining process sequence which does not involve an alkali treatment and the subsequent removal of soapstock is often referred to as "physical refining", and is highly desirable in terms of avoiding pollution, processing simplicity and yield.

The removal of free fatty acids with physical refining occurs by distillation at temperatures above 220 °C.

Besides removal of fatty acids, prior to the hydrogenation of the glyceride oil the phosphatide level should be brought down to a phosphorus content of 4 ppm or less, preferably 2-3 ppm phosphorus or less in order to avoid an inhibition of the hydrogenation catalyst used and/or an interference with the removal of the catalyst by filtration after the hydrogenation. Almost no inhibition of the hydrogenation catalyst occurs with oils containing no more than 4 ppm phosphorus.

It has been disclosed in JAOCS, July 1989, 66, no. 7, page 1002-1009, that so called totally degummed oils, having a very low phosphorus content (lower than 10 ppm, generally 4-7 ppm P), can be successfully hydrogenated even when the usual prior neutralization treatment is omitted.

At the 47. Jahrestagung of the Deutsche Gesellschaft für Fettwissenschaft (2-5 September 1991 in Braunschweig, abstract in Fat.Sci.Technol. 1991, 93, nr. 12, p. 468) it was reported that superdegummed 35 and totally degummed oils could be hydrogenated with very good results even when the oil was not alkali treated or bleached before. The abstract is silent on the way this result has been obtained. It is well known that even without previous bleaching oils can be hydrogenated by increasing the amount of catalyst especially in the case of totally degummed oils with a relatively low phosphorus content.

US-A-4,857,237 discloses a process for refining oil, in which an effective aqueous substance is used so that after hydrogenation using a nickel catalyst, subsequently residual nickel may be removed by filtration. 40 This aqueous substance, such as water, steam or a diluted aqueous acid, may be added prior, during or after hydrogenation. Improved filtration results are obtained because of the agglomeration of finely divided nickel catalyst particles. The amount of aqueous substance added is dependent on the water content of the glyceride oil used.

US-A-4,179,454 discloses a two-step process for providing completely hydrogenated fatty acids. In a first step crude or unrefined glyceride oil is subjected to a catalytic hydrogenation, and in a second step the hydrogenated glyceride oil obtained is split into hydrogenated fatty acids and glycerine. Prior to the hydrogenation the crude glyceride oil may be subjected to a cumbersome degumming process, such as a treatment using water, boric acid, sodium chloride and the like, in order to decrease the phosphatide 50 content of the crude oil. Subsequently, the oil may be dried, and alternatively, a preferred catalyst system comprising two types of catalysts may be used in order to obtain completely hydrogenated fatty acids.

It has now been found that a direct, selective and partial hydrogenation process is possible for glyceride oils containing phosphatides having a phosphorus content up to 60 ppm P without the need of a pre-refining treatment aimed at lowering the phosphorus content. Accordingly, the production of loaded bleaching earth and the use of chemicals is minimized or even avoided. The object of the invention is to provide a 55 hydrogenation process for not pre-refined oils containing up to 60 ppm P.

These objectives are obtained with a hydrogenation process characterised by a positive control of moisture content of the reaction mixture which according to the present invention comprises the steps of:

- i) selecting a glyceride oil comprising less than 60, preferably less than 40 mg P/kg oil;
- ii) carrying out the hydrogenation treatment by
 - a) contacting the glyceride oil with hydrogen in the presence of a hydrogenation catalyst
 - b) saturating partially the initially available double bonds in the glyceride oil; and
 - c) removing the catalyst;

wherein the steps a-c are carried out under such conditions, that the water content of the oil comprising mixture is less than 0.2% by weight calculated on the weight of the oil comprising mixture; and

- iii) optionally purifying the hydrogenated oil from remains of catalyst.

It is decisive for the hydrogenation process of the present invention that the hydrogenation treatment is carried out in substantial absence of water, so that the precipitation of phosphatides is avoided. Precipitation is avoided when the water content is less than 0.2% by weight. Good results are obtained with a water content of 0.005-0.15% by weight. If the phosphorus content is so low that precipitation is not likely, even in the presence of moisture, it still is advantageous to hydrogenate under dry conditions because the adverse effect of water on the catalyst is avoided.

If the moisture content of the available oil is 0.2% by weight or higher, it can be dried in the usual way, e.g. by heating it at a temperature over 100 °C, preferably 120-140 °C. The moisture content can be further decreased by sparging the oil with an inert gas, for example nitrogen. Especially when using fixed bed hydrogenation where the catalyst should be spared as much as possible a very low moisture content is desired.

Performing the hydrogenation treatment according to the invention at such a low water content involves also a positive control of the dryness of the hydrogen which is used in the hydrogenation treatment in up to a 70-fold excess over the oil volume. Suitable dry hydrogen comprises hydrogen produced in the so-called pressure-swing process. The positive control of the hydrogen dryness includes further that, when hydrogen is recycled, contact of hydrogen with water is avoided. This means, that in safety locks water may not be used.

Hydrogen pressure generally is 0.1-10 bar. On account of a higher solubility of hydrogen in dry oil the speed of hydrogenation is increased.

Under steady state conditions the water content during hydrogenation lies within the range of 0.005 to 0.15%, but optimal results are obtained in the lower range of 0.01 to 0.1% by weight.

The hydrogenated glyceride oil is used in the production of margarines and shortenings. A minimum level of unsaturation therefore is recommended. Preferably not more than 50% of the initially available double bonds in the fatty acid units of the glyceride oil will be saturated. However, superior products are obtained when not more than 70% of the initially available double bonds are saturated.

When the hydrogenation treatment is carried out at a moisture content of less than 0.2% by weight, the temperature during the hydrogenation treatment may be 90-220 °C, generally is above 120 °C, but preferably is within the range of 150-220 °C. At that temperatures there is no substantial adverse effect on the hydrogenation by the phosphatides still present in the glyceride oil.

The hydrogenation catalyst is chosen from catalysts known in the art, and preferably is a partially de-activated nickel catalyst, such as a sulfur poisoned nickel catalyst. The nickel content generally is 15-25%. Suitable partially de-activated catalysts are disclosed in EP-A-0,246,366. The catalyst preferably comprises a mixture of fresh catalyst and recycled catalyst. Preferably the recycling value, that is the ratio of the amount of recycled catalyst over the amount of fresh catalyst, is larger than 5, more preferably within the range of 7-15. Recycling of the catalyst is desired not only for economic reasons, but also because a recycled catalyst enables a more selective hydrogenation. An effect of selective hydrogenation is that the hardened oil contains not more than one stearic acid group.

Generally, the amount of nickel catalyst used for an effective hydrogenation is 0.03-0.8 kg nickel/ton glyceride oil, but lower amounts of 0.05-0.15 kg nickel/ton glyceride oil are attainable with good result. In establishing the figures for catalyst consumption recycling of the catalyst has been taken into account. Therefore the figures reflect the amount of catalyst which has to be replenished to maintain catalytic activity.

The starting oil should have less than 60, preferably less than 40 ppm P. Optimal results are obtained if the starting glyceride oil comprises 15-40 mg P/kg, more preferably 18-35 mg P/kg.

Because with normal separation methods remains of catalyst may stay in the oil, an additional purification step may be necessary.

When appropriate, the hydrogenated oil, freed from catalyst, may be subjected to steam distillation or stripping in order to remove free fatty acids still present in the oil.

The process of the invention is equally applicable to the hydrogenation of phosphatides containing fatty acids. Inhibition of the catalyst is prevented when the moisture content of the reaction mixture is positively

controlled. The moisture content is not allowed to rise above the lowest concentration where phosphatides separate at the hydrogenation temperature.

The hydrogenation process of the present invention will be illustrated by several experiments, given for illustrative purposes and not as a limitation of the invention.

Experiment 1 and 2

Super-degummed sunflower oil (18-25 mg P/kg), super-degummed bean oil (30 mg P/kg) and super-degummed rape oil (23-32 mg P/kg and having a water content of 0.1 wt.%) have been subjected to a direct hydrogenation process according to the invention at a hydrogenation temperature of 120°/190° C. Nickel catalyst containing 15% nickel (C-cat obtained from Unimills, Zwijndrecht, the Netherlands), was used in an amount of 0.42 and 0.53 kg catalyst/ton oil, respectively, corresponding with 0.06-0.08 kg nickel/ton oil. The recirculation value was 12 and 10, respectively. During hydrogenation the moisture content was controlled at 0.1 wt% of the mixture under hydrogenation.

These results show that using glyceride oils having a phosphorus content up to 32 mg P/kg had no adverse effect on the catalytic hydrogenation at a catalyst usage of only 0.5 kg catalyst (0.075 kg nickel)/ton oil at a recycling value of about 10-12.

Experiment 3

Super-degummed sunflower oil of the same quality as used in experiment 1 and 2 was subjected to a hydrogenation process according to the invention. The hydrogen pressure was 3 bar. The total hydrogen consumption was 320 m³ per 10 ton, and the hydrogen recirculation was 50 m³/hour. Fresh nickel catalyst was used (C-cat available from Unimills, Zwijndrecht, the Netherlands).

The results are shown in the table 1 below.

Experiment 4

Super-degummed sunflower oil of the same quality as used in experiment 1 and 2 was subjected to a direct hydrogenation process according to the invention using fresh nickel catalyst (P9908 obtained from Unichema, Emmerich, Germany), or a double amount of used catalyst initially used in experiment 3. The results obtained are shown in the table 1 below.

Experiment 5

Super-degummed rape oil of the same quality as used in experiment 1 and 2 was subjected to a direct hydrogenation process according to the invention using a used P9908 nickel catalyst initially used in experiment 4. The results obtained are shown in the table 1 below.

Experiment 6

Super-degummed bean oil of the same quality as used in experiment 1 and 2 was used in a direct hydrogenation process according to the invention using either fresh C-cat (obtained from Unimills, Zwijndrecht, the Netherlands) or 3-7 times the amount of nickel catalyst initially used in experiment 3. The results obtained are shown in the table 1 below.

Experiment 7

Super-degummed rape oil of the same quality as used in experiment 1 and 2 was subjected to a direct hydrogenation process according to the invention using either a fresh nickel catalyst of the type C-Kata or 3-7 times the amount of catalyst initially used in experiment 3. The results obtained are shown in the table 1 below.

Experiment 8

10 tons of superdegummed sunflower oil was hardened at 130-150° C with 0.18% fresh catalyst (Pricat 9920™) (corresponding with 0.04% nickel) at a pressure of 3 bar absolutely dry hydrogen. After an uptake of 330 m³ hydrogen sunflower oil hardened to a melting point of 22° C was obtained.

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One batch (A) having a moisture content controlled at 0.17% was hydrogenated as such. Another batch (B) was heated until 130 °C and kept at a vacuum of 80 mbar, resulting in a decrease of moisture to 0.05 wt.%. See for the hardening times of the two batches Table 2.

5 Experiment 9

500 g of superdegummed soya bean oil (15 ppm P) was hardened at 140 °C and at a pressure of 3 bar absolutely dry hydrogen with fresh Pricat 9910™ catalyst, corresponding to 0.04 % nickel, until the refractive index n_D^{65} of the oil had decreased from 1.4583 to 1.4542.

10 In order to establish the effect of previous drying on hardening time four batches of oil mixed with catalyst were subjected to different pre-treatments before at 140 °C hydrogen was introduced in the reaction mixture:

Batch A was heated until 140 °C under nitrogen in a closed system.

Batch B was heated until 140 °C under vacuum.

15 Batch C was heated until 90 °C and kept under vacuum during 30 min. and then heated to 140 °C under nitrogen.

Batch D was heated until 140 °C and kept under vacuum during 30 min.

See for hardening times Table 3.

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Table 1

	Experiment						
	3	4	5	6	7		
Water content (wt%) controlled at	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Hydrogenation temperature (°C)	120-140	140-150 175-185 ¹⁾	140-150 175-185 ²⁾	120-140	120-140	120-140	120-140
T ₁	--	--	--	--	--	--	--
T ₂	--	--	--	--	--	--	--
Catalyst activity	100	5-20	10	80-100	80-100	80-100	80-100
IV	97±102	58-69	about 75	98-105	about 91	about 91	about 91
Trans index	23± 3	54± 5	65± 7	20± 2	about 30	about 30	about 30
Linoleic acid (%)	<30	--	--	--	--	--	--
Slip melting point (°C)	<25	43± 1	35± 1	<30	≤28	≤28	≤28
Solids (%) at:							
15°C	5- 8	86-92	74-79	5- 8	5-8	5-8	5-8
20°C	3- 5	77-83	57-62	2- 5	2-5	2-5	2-5
25°C	1- 3	64-70	35-40	1- 2	1-3	1-3	1-3
30°C	0- 1.5	47-53	16-21	0- 1.5	0-1.5	0-1.5	0-1.5
35°C	0- 0.5	27-32	3- 6	0- 0.5	0-0.5	0-0.5	0-0.5
40°C	0	11-15	--	0	0	0	0
Refractive index (RI) at 40°C	1.4635	1.4596-1.4600	1.4609-1.4611	1.4638-1.4645	about 1.4635	about 1.4635	about 1.4635

¹⁾ after RI = 1.4643-46

²⁾ after RI = 1.4635-38

Table 2

Hardening of superdegummed sunflower oil		
Batch	Moisture content (wt%) controlled at	Hardening time (min.)
A	0.17	144
B	0.05	72

Table 3

Hardening of superdegummed soya bean oil		
Batch		Hardening time (min.)
A	140 °C, nitrogen	154
B	140 °C, vacuum	134
C	30 min, 90 °C, vacuum then 140 °C, nitrogen	128
D	30 min., 140 °C, vacuum	120

Claims

1. Hydrogenation process for unsaturated glyceride oil comprising the steps of:
 - i) selecting a glyceride oil comprising less than 60 mg P/kg oil;
 - ii) carrying out the hydrogenation treatment by
 - a) contacting the glyceride oil with hydrogen in the presence of a hydrogenation catalyst
 - b) saturating partially the initially available double bonds in the glyceride oil and
 - c) removing the catalyst;
 wherein the hydrogenation treatment being positively controlled by intentionally maintaining the moisture content of the reaction mixture comprising oil, hydrogenation catalyst and hydrogen, below 0.2% by weight calculated on the weight of the mixture; and
 - iii) optionally, purifying the hydrogenated oil from remains of catalyst.
2. Process of claim 1, wherein the controlled moisture content of the mixture is 0.005-0.15% by weight.
3. Process of claims 1-2, wherein the controlled moisture content of the mixture is 0.01-0.1% by weight.
4. Process of claims 1-3, wherein the selected oil comprises less than 40 mg P per kg oil.
5. Process of claims 1-4, wherein the selected oil comprises 15-40 mg P per kg oil.
6. Process of claims 1-5, wherein the selected oil comprises 18-35 mg P per kg oil.
7. Process of claims 1-6, wherein not more than about 50%, preferably not more than 70% of the initially available double bonds are saturated.
8. Process of claims 1-7, wherein the hydrogenation is carried out at a temperature above 120 °C, preferably at a temperature of 150-250 °C.
9. Process of claims 1-8, wherein the catalyst comprises partially deactivated nickel catalyst.
10. Process of claims 1-9, wherein the catalyst removed in step ii-c is recycled.
11. Process of claim 10, wherein the recycling value of the catalyst is larger than 5, preferably 7-15.

12. Process of claims 1-11, wherein the amount of catalyst used is about 0.03-0.8 kg nickel/ton glyceride oil.

5 13. Process of claims 1-11, wherein the amount of catalyst used is about 0.05-0.15 kg nickel/ton glyceride oil.

14. Process of claims 1-13, wherein the hydrogenated oil purified from catalyst is subjected to steam distillation or stripping with an inert gas.

10 15. Hydrogenation process for unsaturated fatty acids which comprises contacting the fatty acids with hydrogen in the presence of a hydrogenation catalyst, characterised by a positive control of the process by intentionally maintaining low the moisture content of the reaction mixture comprising fatty acids, hydrogenation catalyst and hydrogen.

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